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Metallurgical Effects of Impurities in Recycled Copper Alloys

By Harry V. Makar and William D. Riley

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

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CONTENTS

	Page
Abstract	1
Introduction	2
Effects of impurities on copper alloys	4
Wrought alloys	6
Cast alloys	6
Metallurgical effects of tramp elements	8
Hot workability	8
Effect of lead	9
Effect of lead and iron	9
Effect of lead and zirconium	11
Fire cracking	11
Effect of chemistry and processing	12
Liquid metal embrittlement	12
Additional studies	13
Microstructural effects	14
Tin bronzes	14
Metallography	14
Base alloy	14
Antimony	14
Iron	14
Lead	14
Nickel	14
Phosphorus	15
Silicon	15
Sulfur	15
Microprobe analysis	15
Iron	15
Nickel and antimony	15
Sulfur	15
Tin	15
Zinc	15
Grain size and shape	15
Eutectoid composition	15
Microsegregation	16
Failure analysis of bronze propellers	16
Composition	16
Results of analysis	16
Summary	17
References	18

ILLUSTRATIONS

1.	Typical sorting routine for mixed copper alloy scrap	4
2.	Schematic representation of grain boundary voids due to dislocation impingement on grain boundary impurities	9
3.	Effect of lead, iron, and iron and lead on hot rolling of 60:40 brass	10
4.	Effect of iron on hot rolling of a complex brass containing 1.33 pct Mn	10
5.	Effect of lead and iron on hot rolling of a complex brass at 650° C	10
6.	Effect of lead and iron on hot rolling of a complex brass at 800° C	11
7.	Effect of zirconium and lead on hot twist ductility of a copper-nickel alloy	11
8.	Effect of lead on tensile ductility (reduction in area) of nickel-silvers	13
9.	Effect of lead on stress-strain behavior of nickel-silvers	13

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TABLES

		Page
1.	Typical copper alloys, nominal composition	3
2.	Compositional variations for wrought and cast copper alloys	5
3.	Limits for lead and bismuth in alpha copper alloys for hot rolling	6
4.	Effect of impurities on phosphor bronzes	7
5.	Effect of chemical composition on fire cracking	12
6.	Composition of tin bronze alloy used for microstructure studies	14
7.	Chemical composition of propeller blades	16

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

HB	Brinell hardness number	pct	percent
in	inch	ton/in^2	ton per square inch
kg/mm^2	kilogram per square millimeter	wt pct	weight percent
mm	millimeter		

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METALLURGICAL EFFECTS OF IMPURITIES IN RECYCLED COPPER ALLOYS

By Harry V. Makar [1] and William D. Riley [2]

ABSTRACT

As part of a continuing research program for conserving domestic mineral resources, the Bureau of Mines is investigating new and improved scrap identification techniques to improve sorted mixed scrap purity. This report focuses on various classes of wrought and cast copper alloys produced with recycled scrap. Based on a survey of the literature, principal alloys, such as the brasses and bronzes, are examined with respect to impurity elements and their effects on metallurgical behavior. Effects of elements such as lead, antimony, iron, chromium, and aluminum are discussed. The metallurgical effects described include hot shortness, fire cracking, and undesirable phase transformations.

[1]Branch Chief, Division of Ferrous Metals, Bureau of Mines, Washington, DC.

[2]Physical science technician, Bureau of Mines, Avondale Research Center, Avondale, MD.

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INTRODUCTION

Old scrap was 26 pct of the total 2,278,000 metric tons of U.S. copper supply in 1981 and is expected to be about 29 pct by 2000 (4).[3] The smelters and refiners consumed 54 pct of the total, brass mills 40 pct, and others 6 percent. Overall, the secondary metals industry consists of an estimated 4,000 dealers and scrap processors. Details on secondary copper are available in other publications by the Bureau of Mines and the National Association of Recycling Industries (NARI) (5, 21, 23-24, 30-32).

Specifications for the various alloys produced by the industry dictate the quality and the extent of upgrading and refining that may be required. In some cases, refining may be too costly or impractical and the need for highly segregated scrap is essential. It has been estimated that at one time as many as 500 commercial copper alloys were made in the United States. With such a large number of alloys and the almost infinite varieties of mixtures that can occur when these alloys come back into the recycling process, the task of proper upgrading is indeed monumental. This task is greatly lessened with the use of classifications such as those published by the National Association of Recycling Industries (24). These classifications provide a standardized system for use by the industry to segregate mixed copper alloy scrap into recyclable categories.

Several routine techniques are traditionally used in the copper recycling industry to identify scrap for effective segregation. These include identification based on object recognition, color, apparent density, magnetic attraction, and chemical spot tests. Some of the more sophisticated techniques commercially available include fluorescent X-ray spectroscopy, portable optical emission devices, and thermoelectric sorters. Table 1 lists some common alloy groups and typical compositions compiled by the Institute of Scrap Iron and Steel (ISIS), and figure 1 shows a typical scheme for routine sorting of a mixture of copper alloys. These techniques, when properly applied by skilled sorters to mixtures of these alloys, permit effective identification and segregation into their respective specified categories, such as red brass, yellow brass, manganese bronze, and aluminum bronze.

Although traditional routine sorting methods are effective with regard to generic or descriptive specifications, there are many opportunities for introduction of impurities into new alloys made from improperly segregated scrap. Color distinctions may be obscured under certain lighting conditions. Also, there may be several specific alloys within a certain group, differing significantly in lead, antimony, aluminum, and other elements that cannot be distinguished in routine sorting. In addition to the large number of alloys that must be handled, certain attachments to postconsumer parts also introduce impurities. These include iron fittings and plated parts. Previous Bureau of Mines research (3, 19-20, 25, 27) reported on improved techniques for metal scrap identification. The objective was to develop relatively simple, rapid techniques requiring few operator skills that would improve scrap purity during sorting.

The purpose of this paper is to examine some of the reported metallurgical effects of impurities in copper alloys. Based on the literature, a general overview of reported effects is given for various impurities. This is followed by specific case studies in which the metallurgical effects of selected impurities are examined in more detail. The effects discussed include hot shortness, fire cracking, and unwanted phase transformations. It should be noted that not all of the metallurgical effects are attributable solely to composition. In some cases, the mechanisms of the problems encountered are still not fully understood, and in other cases improper metallurgical processing in terms of foundry control and/or heat treatment may be more to blame than the presence of impurities.

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

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TABLE 1. - Typical copper alloys, nominal composition, weight percent

Alloy	Cu	Sn	Pb	Zn	Others	Common uses
Silicon bronze..	82.5-97	0-1	Trace	13	1.35-4.50 Si	Rod, bar, plate sheet, bearings, impellers, pump parts, valve stems, corrosion-resistant castings.
Red brass.....	85	5	5	5	NAp	General casting for good machining qualities, low-pressure valves, pipe fittings, small pump castings, ornamental fixtures.
Phosphorous bronze.	95	5	NAp	NAp	NAp	Bars, spings, rods.
Navy brass.....	88	6-8	0-2	4	NAp	Steam pressure castings, valve bodies, pipe flange, gears and bushings, pump impellers, steam fittings, valves and parts.
Yellow brass....	66	1	3	30	NAp	Light casting not subject to high internal pressure, hardware fittings, ornamental castings, gas cocks, radiator fittings.
Muntz metal.....	60	NAp	NAp	40	NAp	Large nuts and bolts, brazing rods, condenser tubes.
Admiralty brass.	70	1	NAp	29	NAp	Condenser tubes.
Manganese bronze	59	.25	.25	38	1 Fe 1 Al 0.5 Mn	Valve stems, marine castings and propellers, gears, bushings and bearings.
Aluminum bronze.	88	NAp	NAp	NAp	2 Fe 10 Al	Acid-resistant pumps, valve seats, gears, bushings and bearings.
Copper-nickel...	70 -90	NAp	NAp	NAp	10-30 Ni	Boiler tubes, saltwater equipment.
Nickel-silver...	60 -65	0-5	0-7	NAp	5-25 Ni	Hardware fittings, valves, plumbing fixtures, ornamental castings, dairy and citrus machinery.

NAp Not applicable.

Source: Institute of Scrap Iron and Steel, Inc.

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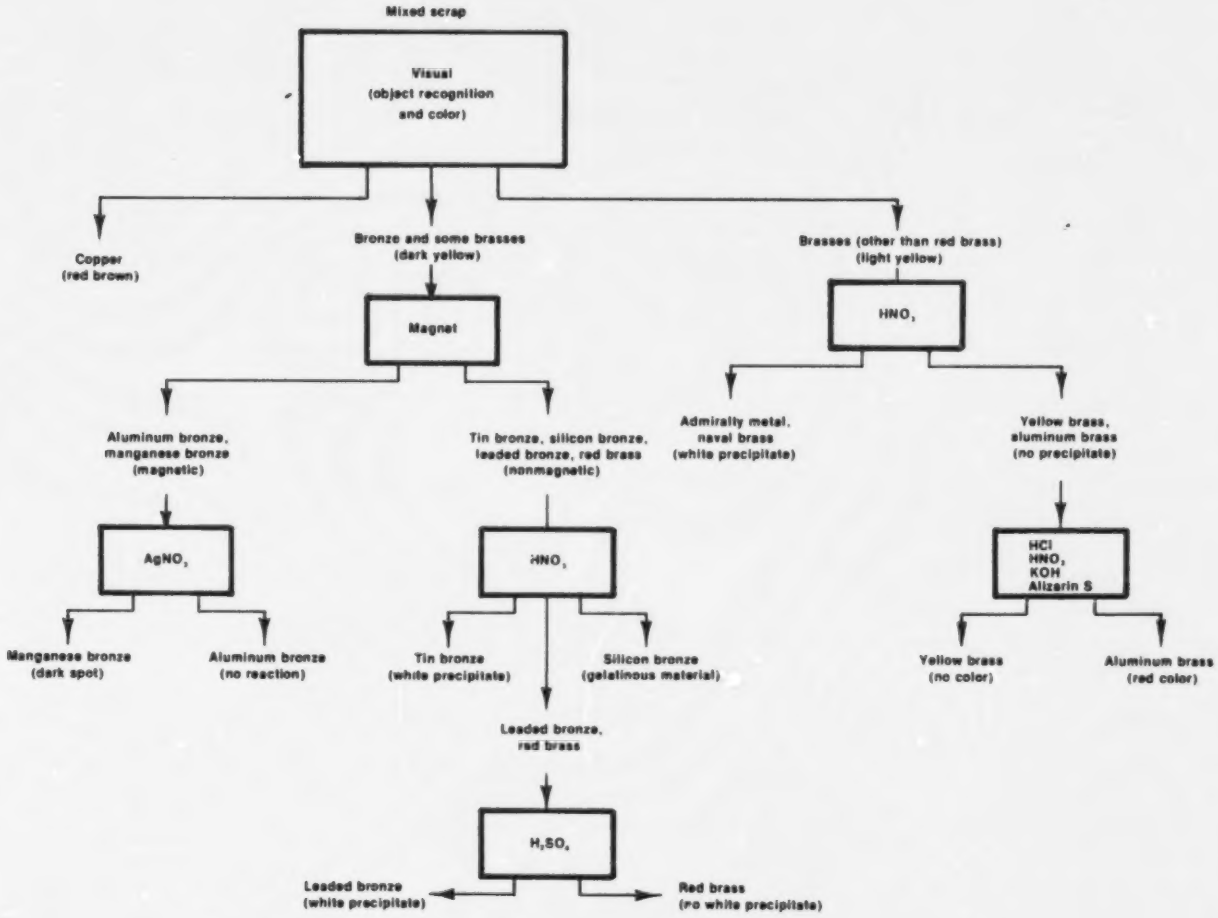

FIGURE 1. - Typical sorting routine for mixed copper alloy scrap.

EFFECTS OF IMPURITIES ON COPPER ALLOYS

A standard designation system for copper and copper alloys has been published by the Copper Development Association, Inc. (7). Approximately 12 pages of wrought and cast copper alloys are listed under various families within the following four general classes: Brasses, bronzes, copper-nickels, and nickel-silvers. Table 2 lists typical alloy families and their compositions. Many of these alloy families also have high-lead versions. Even within given families of alloys (e.g., brasses, bronzes, etc.), there are wide ranges for many elements that can cause metallurgical problems, singly or through interaction effects, if recycled scrap is improperly mixed. Most of these elements are intentionally added to impart certain desired properties in the original alloys. For example, antimony, arsenic, and phosphorus are added in small amounts to wrought alloys to inhibit dezincification; lead to enhance machinability and to promote smooth edges during shearing and blanking operations; tellurium, selenium, and sulfur for improved machinability; aluminum for resistance to impingement corrosion in condenser tubing alloys; and chromium to form a heat-treatable alloy (18). Some of these elements are also used in cast alloys for the same reasons. In

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TABLE 2. - Compositional variations[1] for wrought and cast copper alloys, weight percent (7)

Alloy	Cu	Pb	Al	Sn	Zn	Si	Others
Wrought brasses:							
Yellow brass.....	61-68.5	0.07- 0.15	NAp	NAp	Bal	NAp	0.07 Fe.
Tin brass.....	79-96	.05- .1	NAp	0.2- 3.0	2.0 -20.0	NAp	0.05 Fe, 0.35 Mn, 0.10 As, 0.10 Sb, 0.35 P.
Leaded brass.....	59-90.5	.3 - 3.7	NAp	NAp	Bal	NAp	0.35 Fe, 0.25 As, 1.2 Ni, 0.10 P.
Naval brass.....	59-65	.2 - 2.2	NAp	.5- 1.0	Bal	NAp	0.10 Fe, 0.10 Sb, 0.10 As, 0.10 P.
Wrought bronzes:							
Aluminum bronze...	79-96	0 - .10	2.3-13.5	.2- 2.0	0 - .8	0 -2.2	0.10-5.0 Fe, 0.5-3.5 Mn, 0.5-5.5 Ni, 0.35 As.
Silicon bronze....	94-97	.2 - .8	.1	0 - 1.6	0 - 1.5	.4-4.0	0.1-0.8 Fe, 0-1.5 Mn, 0-2.2 Ni.
Manganese bronze..	55-68	.2 - 3.0	0 - 6.0	0 - 1.5	Bal	0 -1.5	0-2.3 Ni, 0.05-5.0 Mn, 0-4.0 Fe, 0-0.8 As.
Copper-nickel.....	Bal	0 - .05	NAp	NAp	0 - 1.0	NAp	2-33.0 Ni, 0-2.5 Mn, 0-2.3 Fe, 0-3.0 Cr, 0-0.7 Be.
Nickel-silver.....	42-74	0 - 2.0	NAp	0 - .6	Bal	NAp	7.0-26.0 Ni, 0.05-1.0 Mn, 0.25-6.0 Fe.
Cast brasses:							
Red and semi-red.. brass.	75-94	.5 - 8.0	.005	.2- 6.5	1.0 -17.0	.005	0-1.0 Ni, 0-0.4 Fe, 0-0.25 Sb, 0-0.05 P.
Yellow brass.....	57-74	.2 - 3.8	0 - .55	.2- 2.0	20.0 -41.0	0 - .25	0-0.7 Fe, 0-0.20 Sb, 0-0.05 As, 0.2-1.0 Ni, 0-0.25 Mn.
Cast bronzes:							
Manganese bronze..	53-68	.2 - 1.5	.5- 7.5	.2- 1.5	22 -42	NAp	0.1-5.0 Mn, 0-4.0 Ni, 0.4-4.0 Fe.
Silicon bronze....	79-89	.15- 1.0	0 - 1.5	0 - 1.0	5.0 -16.0	1.0-5.5	0-2.5 Fe, 0-1.5 Mn, 0-0.06 As, 0-0.06 Sb, 0-0.06 P.
Tin bronze.....	79-94	.20- .50	.005	6.0-20.0	.25- 5.0	.005	0.10-0.25 Fe, 0.20 Sb, 0.05-1.0 P, 0-0.1 Mn.
Aluminum bronze...	[2]71-86	0 - .03	6.0-11.5	NAp	NAp	0 -3.3	0-5.0 Fe, 0-14 Mn, 0-5.5 Ni.
Cast nickel-silver..	53-67	1.0 -11.0	0 - .005	1.5- 5.5	1.0 -25.0	0 - .15	11.0-27.0 Ni, 0.5-1.0 Mn, 0-0.35 Sb, 0-0.05 P, 1.5 Fe.

Bal Balance.

NAp Not applicable.

[1]Constituent figures are maximums except where shown as a range or otherwise specified. Composition ranges represent more than 1 specific allow within a group.

[2]Minimums.

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5

addition, lead is added to produce bearing alloys; iron, silicon, and aluminum may be used to provide improved mechanical properties; phosphorus and boron (as well as silicon) are used as deoxidizers (18). Mixing high-lead scrap with an otherwise similar alloy (dilution with cathode copper) would be particularly costly in alloy applications where hot workability demands very low lead concentrations. In general, cast copper alloys can tolerate higher impurity levels than wrought alloys since they are not subjected to mechanical working. Typically, impurities in wrought alloys affect work response (e.g., hot and cold shortness) or thermal response (e.g., recrystallization, fire cracking), while in cast alloys impurities generally affect castability, soundness, and physical properties.

WROUGHT ALLOYS

Wrought alloys are generally hot-worked above the recrystallization temperature of the alloy and thus are free from the strain-hardening effects associated with cold working. Cold working is normally done below recrystallization temperatures. Foulger (12) has discussed impurity effects on hot and cold workability in copper alloys. In cold working, impurities that affect the amount of the relatively hard and brittle beta phase must be carefully controlled. As a general rule, beta and alpha plus beta alloys are more easily hot worked, even in the presence of impurities, while single-phase alpha alloys require a much higher purity level. Hot shortness in wrought alloys is caused by such low-melting elements as lead, antimony, and bismuth and in some cases iron and silicon. Even very low levels of impurities can be detrimental. Bismuth, for example, has been considered detrimental in amounts just sufficient to form a single atom layer along grain boundaries (6, 12, 18). Limits for lead and bismuth based on commercial hot-rolling experience were reported by Jackson (17) for four common copper alloys as listed in table 3.

TABLE 3. - Limits for lead and bismuth in alpha copper alloys for hot rolling, weight percent (17)

Alloy	Pb	Bi
70:30 brass.....	0.02	0.002
Nickel-silver copper.....	.015	.001
Phosphor bronze (95:5).....	.004	.0004

Cold shortness is a loss in ductility in metals worked at temperatures below the recrystallization temperature. Glickman (14) has shown that cold shortness is another intergranual phenomenon caused by extremely low amounts of bismuth, tellurium, antimony, and boron segregated along grain boundaries.

File cracking has also been attributed to low-melting impurities, such as lead, and those that form brittle intercrystalline films, such as bismuth (6, 18). Copper alloys may alternately undergo heat-affected-zone (HAZ) cracking when lead, tellurium, bismuth, or sulfur is present, even though actual fire cracking does not take place (13).

Recrystallization and grain growth are also affected by impurities. For example, Fargette (11) has shown that, at least for relatively simple copper alloys, a few hundred parts per million or less of silver, phosphorus, cadmium, manganese, or tin can increase the recrystallization temperature. Recrystallization is inhibited because impurities segregate in dislocations and grain boundaries, reducing their mobility (8, 10). Impurities have also been shown to affect grain size and orientation (22, 26).

CAST ALLOYS

Cast copper alloys are used for sand casting or chill casting of various components. Typically, alloy additions are made to improve characteristics such as hardness or corrosion resistance. Usually one characteristic is improved at the expense of another. For example, iron is added to some yellow brasses to increase strength at the expense of reduced elongation. Table 2 lists the range of compositions for some principle casting alloys. Elements such as lead and

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antimony, which are in relatively high concentrations in some alloys, could not be tolerated in others. Cast alloys generally can tolerate greater amounts of impurities than wrought alloys. The effect of impurities on cast alloys may also depend on the method of casting, i.e., whether sand cast or chill cast (32). Mechanical properties can be impaired in certain tin bronzes by magnesium, silicon, aluminum, and even zinc. These elements have similar properties in that they form oxide films on the surface of molten bronzes which break up on pouring and cause rough surfaces on the resulting chill-cast products. Because film formation interferes with feeding within the mold, fissure porosity can result, greatly reducing mechanical properties (33). Proper segregation of scrap alloys is also essential in that some silicon bronzes contain small amounts of arsenic and antimony. In bronze castings, arsenic and antimony decrease the solubility of tin, thus increasing and coarsening the brittle delta phase, which impairs the mechanical properties (1-2). Arsenic and antimony concentrations as low as 0.12 and 0.18 wt pct were found to severely reduce the tensile elongation of tin bronzes (32).

In general, the impurities tend to decrease the mechanical properties and castability. It is also possible that impurities such as aluminum and silicon can cause casting voids, which serve as sites for stress corrosion cracking.

Similar effects of impurities on phosphor bronzes, tin bronzes, and their leaded alloys have been reported by Winterton (33) and Stolarczyk (32). For example, table 4 illustrates the effects of aluminum, silicon, iron, lead, and bismuth on a typical phosphor bronze. In general, an increase in impurities decreases tensile strength and elongation, while hardness is variable.

Impurities can also cause microstructural changes in cast copper alloys. For example, grain shape or size can be changed, as in the case of iron in brasses (10). In other cases, solid solutions or compounds are formed. It has also been shown (26) that chromium, although below specified maximum concentrations, can lead to fatigue failure in a manganese-nickel-aluminum bronze alloy (75Cu-12Mn-8Al-2Ni-3Fe). Failure results from chromium segregation and eventual formation of a dendritic phase, leading to coarse grains and weak structure.

TABLE 4. - Effect of impurities on phosphor bronzes (33-34)

	Concentration, wt pct	Tensile strength, ton/in^2	Elongation, pct	Hardness, HB
Standard alloy..	NAp	27.2	18	138
Aluminum.....	0.005	25.3	15	123
	.01	21.8	5	133
	.47	23.2	6	130
Bismuth.....	.32	25.6	14	127
	1.25	23.8	10	126
Iron.....	.28	28.5	15	136
	.80	26.1	11	132
	1.69	22.2	4	139
Lead.....	.24	26.3	15	128
	.70	25.4	15	125
	1.61	23.8	10	126
Silicon.....	.01	26.3	18	119
	.07	24.3	9	131
	.38	24.2	7	138

NAp Not applicable.

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METALLURGICAL EFFECTS OF TRAMP ELEMENTS

The practical aspect of secondary copper alloy production is presumably based on achieving the best corrosion resistance at the lowest cost. Cost in this context refers to both processing and raw material cost. The extent to which relatively low-cost scrap can be utilized to achieve required final quality without excessive processing cost is well understood by the industry. Millions of tons of high-grade products testify to the metallurgical acceptability of recycling. As noted in the above overview section, the effects of certain undesired elements are well understood, and for the most part they are effectively avoided. Some metallurgical problems have arisen, however, where interaction effects among various elements and/or certain microstructural behaviors were not well understood. The following case studies were selected as examples of the perhaps less well known metallurgical effects of impurities in copper alloys and to emphasize the importance of careful scrap sorting and segregation. Some of the examples also illustrate that corrective metallurgical treatments may counteract certain impurities. It is important to note that although impurities are often major problems, certain metallurgical problems are due to factors other than composition.

HOT WORKABILITY

Metallurgical and processing factors associated with the hot workability of brasses, bronzes, copper-nickels, and nickel-silvers have been examined by a number of researchers. Studies by Cook (6), Davies (10), Foulger (12), and Heslop (15) were selected for most of the following discussion. The preceding discussion described various effects of alloying elements and impurities on copper alloys. It is important to note that the literature from which these data were obtained also mentions the use of metallurgical controls (e.g., special alloy additions or processing techniques) to enhance hot workability. Even without harmful levels of impurity elements, improper metallurgical processing can cause hot shortness.

Factors affecting hot workability include crystal structure, soundness, segregation, and composition. The effect of composition is highlighted here to illustrate some of the direct or potential effects of certain impurity elements. Alloys such as brasses, aluminum bronzes, copper-nickels, and silicon bronzes may contain up to 1 or 2 pct of various alloying elements to achieve desired mechanical properties. Except for lead and other low-melting elements, the alloying elements enter into solid solution and generally have little or no effect on hot workability. Interaction effects from impurities at relatively low concentrations can have severe detrimental effects, however, although there seems to be little published on this subject. It is important to note that the quality of the cast ingot prior to working and response to homogenizing soak treatments are extremely important factors affecting hot working. A fine, uniform cast grain structure, for example, generally results in better hot workability and tolerance for impurities than a coarse, nonuniform grain structure. The severity of hot working also determines hot workability, such that a given alloy may fail during hot piercing for tubemaking but form satisfactorily during hot rolling or extrusion. Regarding workability of metals in general, Semiatin (29) gives an excellent description of the action of dislocations and intergranular impurities on the formation of voids at grain boundaries. Secondary tensile stresses develop at the voids during metal working operations, eventually leading to fracture. Figure 2 is a schematic description by Semiatin showing grain boundary voids and dislocation impingement (inverted T's). Figure 2 also depicts triple-junction cracks, which appear at the junction of three grains and subsequently lead to fracture during hot working.

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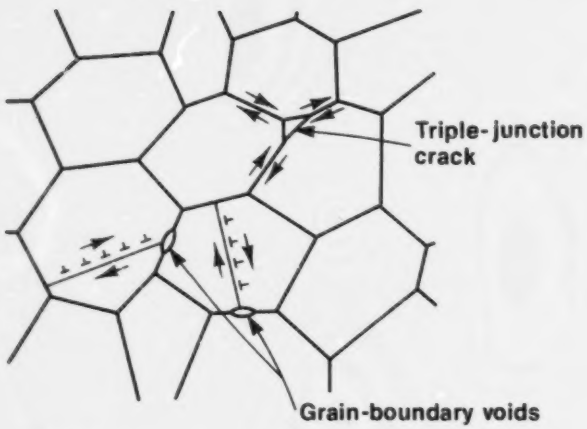

FIGURE 2. - Schematic representation of grain boundary voids due to dislocation impingement on grain boundary impurities. Also shown is a triple junction crack (29).

Effect of Lead

Lead is among the most prevalent and deleterious elements affecting hot workability. The maximum that can be tolerated depends on such factors as overall composition, structure, and processing techniques.

In brasses, lead is harmful at levels as low as 0.01 wt pct. In phosphor bronzes, Jackson (17) showed that 0.004 wt pct lead is considered the maximum tolerable for hot rolling (table 3). In other alloys, lead may be tolerated up to 0.02 wt pct, and even 0.05 wt pct or higher. Extreme care is needed if alloys containing lead for machinability are to be hot-worked. For copper-nickel alloys, bismuth, tellurium, and selenium must be limited to levels as low as 0.001, 0.003, and 0.006 wt pct, respectively (12). The harmful effects of lead (and the other low-melting elements) are attributed to the general characteristics of low melting point and limited solid solubility in the parent alloy. The lead and/or its low-melting compounds segregate along grain boundaries and are liquid at normal hot-working temperatures. Hot shortness may or may not occur, depending on interfacial tensions between the liquid phase and the solid grains of the parent alloy (5, 17, 33). The details of this proposed mechanism are beyond the scope of this paper. As stated earlier, the effect of such impurities may be enhanced or diminished, depending on other factors such as grain size control, other alloying elements, initial cast structure, and processing techniques.

Effect of Lead and Iron

Figure 3 shows the effect of high levels of lead on edge cracking of a 60:40 brass during hot rolling. The alloy used in this study was relatively pure except for lead and showed appreciable cracking at 0.3 wt pct Pb and catastrophic cracking at 1.0 wt pct Pb. The addition of 1.0 wt pct Fe increases the tolerance for lead.

Studies by Davies (10) described the beneficial effects of iron in lead-containing brasses and offered a possible explanation. Figure 4 shows the effect of iron on hot rolling of brass alloys containing approximately 0.8 wt pct Pb (plus 1.3 wt pct Mn and 1.5 wt pct Al). Figures 5 and 6 show the effect of iron in a somewhat different manner, i.e., two iron levels and varying concentrations of lead. The actual mechanism by which the beneficial effect of iron occurs is apparently not fully understood. Davies refers to other investigators who studied cast beta brasses containing 3 wt pct or more aluminum and related the intercrystalline fraction to the segregation of aluminum atoms along grain boundary areas. They felt that aluminum was being replaced by iron atoms, which were less harmful. In the alloys studied by Davies and depicted in figures 4, 5, and 6, the iron was thought to replace the lead atoms. A typical composition of these brass alloys is, in weight percent, 60 Cu, 1 Sn, 1.5 Al, 0.2 Ni, 0.8 Pb, balance Zn. Iron, manganese, and lead concentrations ranged between 0.04 and 1.34, 0.44 and 1.54, and 0.05 and 1.16 wt pct, respectively.

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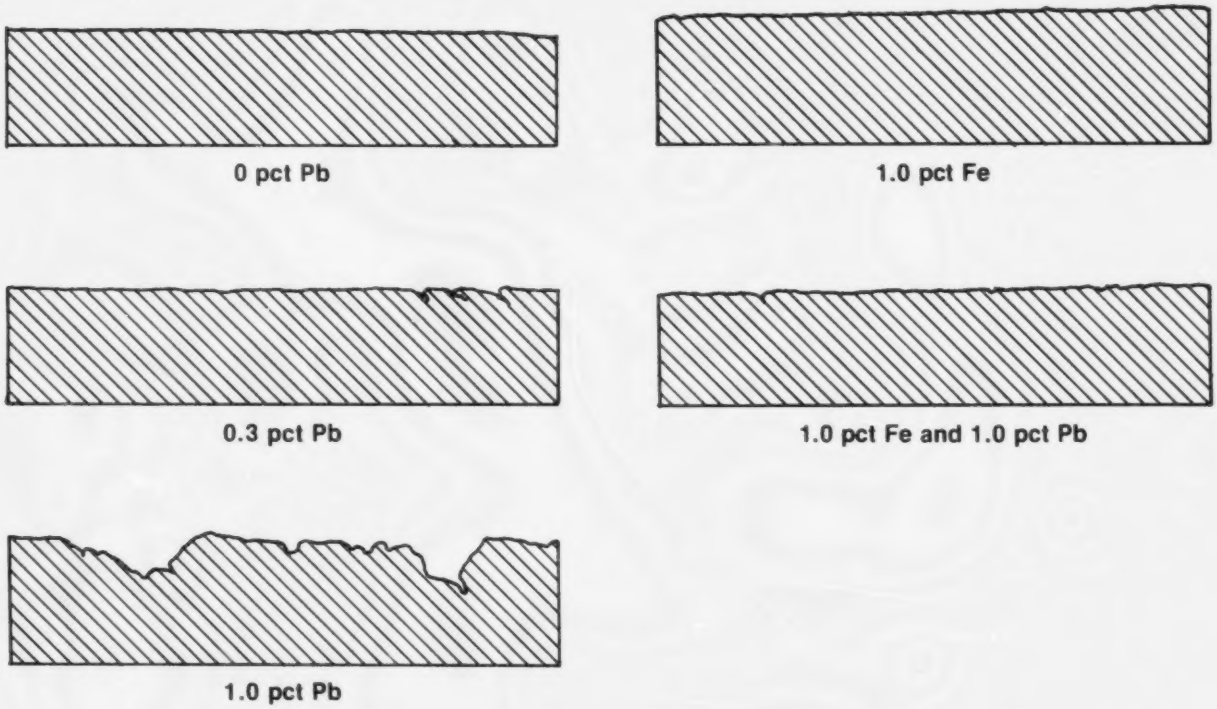

FIGURE 3. - Effect of lead, iron, and iron and lead on hot rolling of 60:40 brass (6).

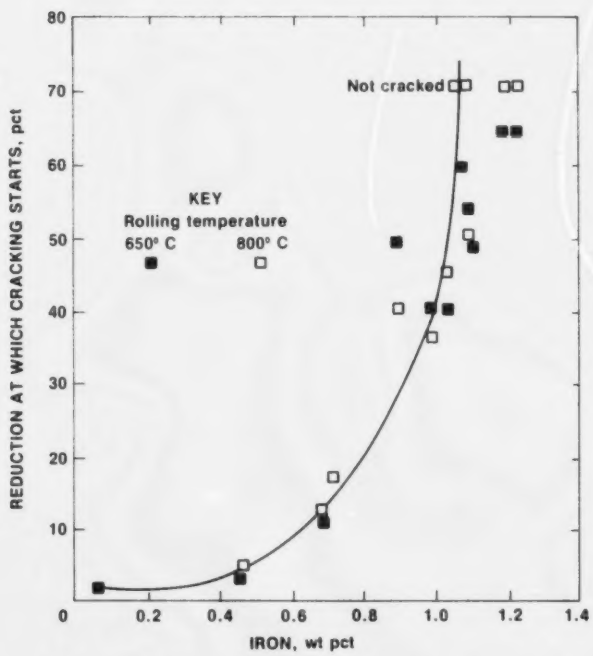

FIGURE 4. - Effect of iron on hot rolling of a complex brass containing 1.33 pct Mn at 650° and 800° C (10).

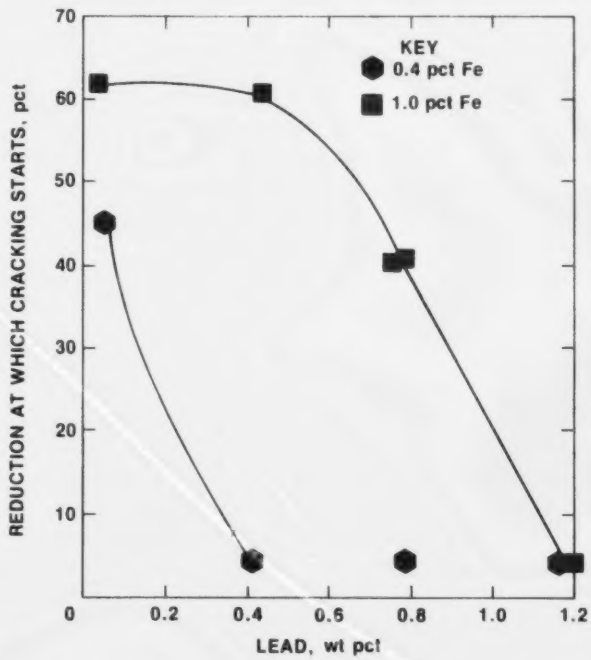

FIGURE 5. - Effect of lead and iron on hot rolling of a complex brass at 650° C (10).

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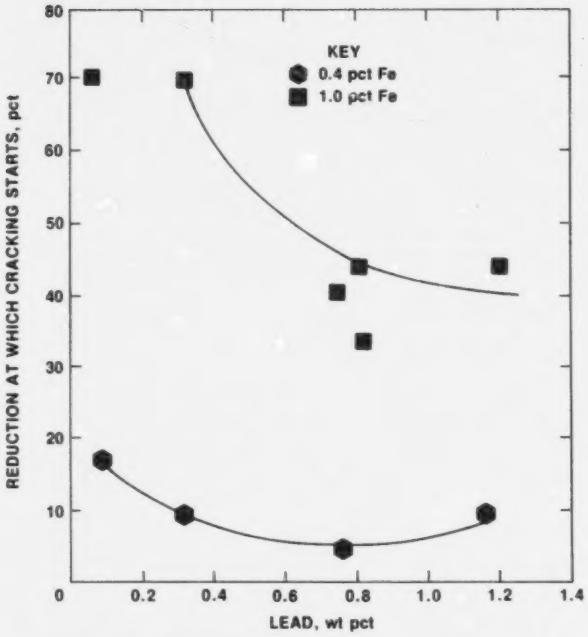

FIGURE 6. - Effect of lead and iron on hot rolling of a complex brass at 800° C (10).

Effect of Lead and Zirconium

Figure 7 illustrates the severe effect of lead on hot ductility of a copper-nickel, and also shows how this effect can be offset by zirconium additions (16). Other studies indicate that approximately 0.05 wt pct Ce and other rare earths can improve the hot workability of copper alloys. The beneficial effects of zirconium are presumably due to pronounced grain refinement, while rare earths, and certain other elements (e.g., thorium, uranium, and lithium) form high-melting intermetallic compounds with lead.

FIRE CRACKING

Fire cracking is a form of embrittlement (cracking) that occurs during rapid heatup to annealing temperatures. This type of cracking has been the subject of a number of studies, yet the mechanism is not fully understood. In one study by Sato (28) fire cracking was investigated for aluminum brass, copper-nickel, and

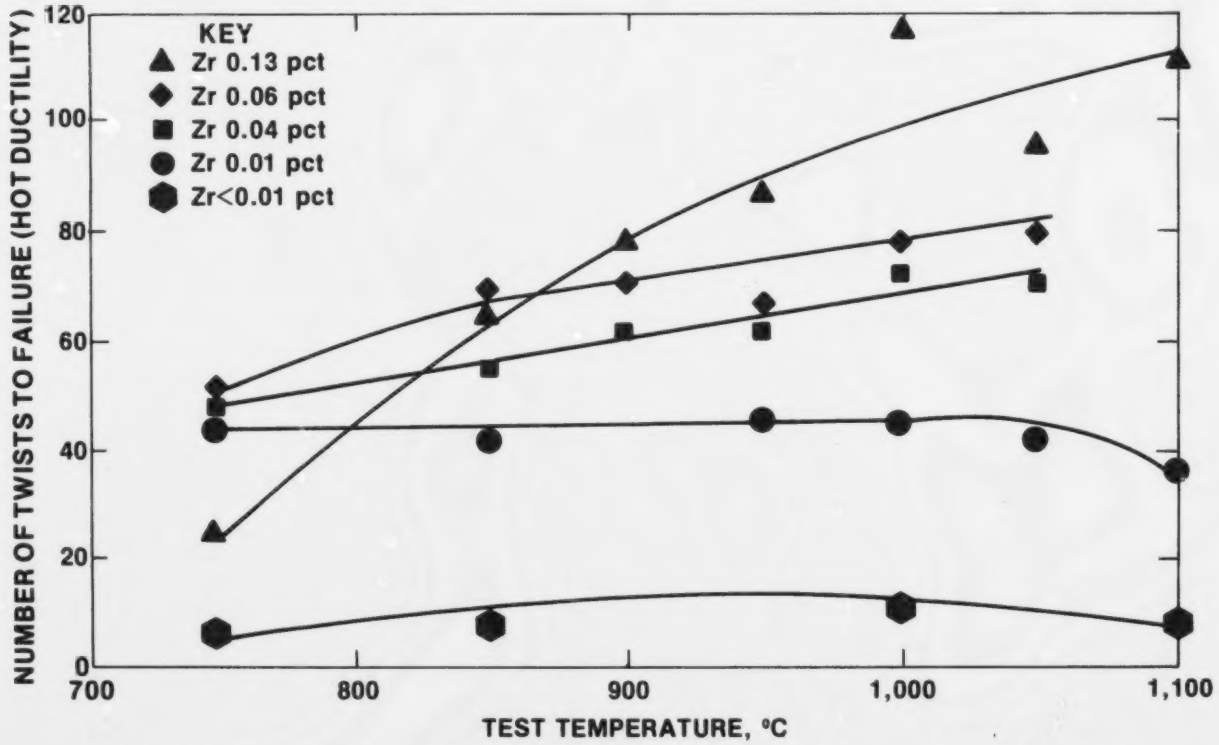

FIGURE 7. - Effect of zirconium and lead on hot twist ductility of a copper-nickel alloy (16).

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chromium-copper. It was concluded that embrittlement occurred as a result of voids along grain boundaries, similar to the behavior observed for alloys subjected to high-temperature creep and tensile tests. The embrittlement due to void formation was further found to be closely related to several factors, including--

1. Magnitude of the residual stress from cold working.
2. Heating rate.
3. Time at temperature.
4. Annealing temperature.
5. Grain size.
6. Reduction ratio during cold working.

The effects of impurities were not described, implying that they were minor compared with the above-mentioned factors.

Effect of Chemistry and Processing

Isler (16) undertook a detailed study to define the mechanism of fire cracking. Table 5 shows results of preliminary tests relating chemical composition to fire cracking. The alpha alloys with lead were clearly prone to fire cracking, whereas the presence of beta phase reduced the tendency. In the absence of nickel, cracking could not be induced. All cracks were intercrystalline. A large number of tests conducted on alloy A revealed that this alloy could exist in a sensitive (to fire cracking) as well as a nonsensitive state after being cold-worked and heat-treated in presumably identical fashion. This observation led to the conclusion that in addition to lead concentration and type of crystal structure, other factors governed sensitivity to fire cracking. Further detailed studies were conducted to examine effects of residual stresses from cold work, the rate of heating, grain size, the role of porosity, and the role of lead. Casting porosity was clearly a major factor rendering alloys sensitive to fire cracking. The effect of lead was studied in considerable detail, providing the major subsequent observations on which a proposed mechanism was based.

TABLE 5. - Effect of chemical composition on fire cracking (16)

Alloy	Composition, wt pct				Phase(s) present	Sensitive to fire cracking
	Cu	Zn	Ni	Pb		
A....	62	19	18	1	α	Yes
B....	62	20	18	0	α	No
C....	62	24	13	1	α	Yes
D....	53	38	8	1	α	Yes
E....	47	41	10	2	α and β	No
F....	51	42	6	1	α and β	No
G....	71	28	ND	1	α	No

Liquid Metal Embrittlement

Hearing tests on alloys A and D, table 5, revealed that both alloys cracked at 318° C, slightly lower than the melting point of lead (327° C). Microprobe analysis showed that lead particles contained the main alloying elements of the matrix (copper, zinc, and nickel). This and the fact that lead is known to form low-melting eutectics with these elements (e.g., 318° C with 0.5 wt pct Zn) supported the conclusion that the fire-cracking temperature coincided with the melting point of the lead particles. The fire-cracking temperature was found to be independent of the matrix composition. Liquid metal embrittlement was thus suspected as being responsible for fire cracking, and a series of tensile tests were run to show whether alpha nickel-silver and lead formed an embrittling couple. Figure 8 shows tensile ductility (reduction of area) for alloys A, B, and F at various temperatures. These results (and supporting Charpy impact tests) showed a marked drop in ductility at about 300° C for alloy A, but not for alloy B (which is the same as alloy A but without lead). A ductility minimum also occurred at about 300° C for all alloys, owing to spontaneous strain aging for the alpha-phase alloys (A and B) and to intercrystalline cavity formation for the alpha-beta alloy F. Figure 9 shows strain-aging embrittlement as evidenced by the serrations in the stress-strain curve of alloy B but shows no serrations for alloy F.

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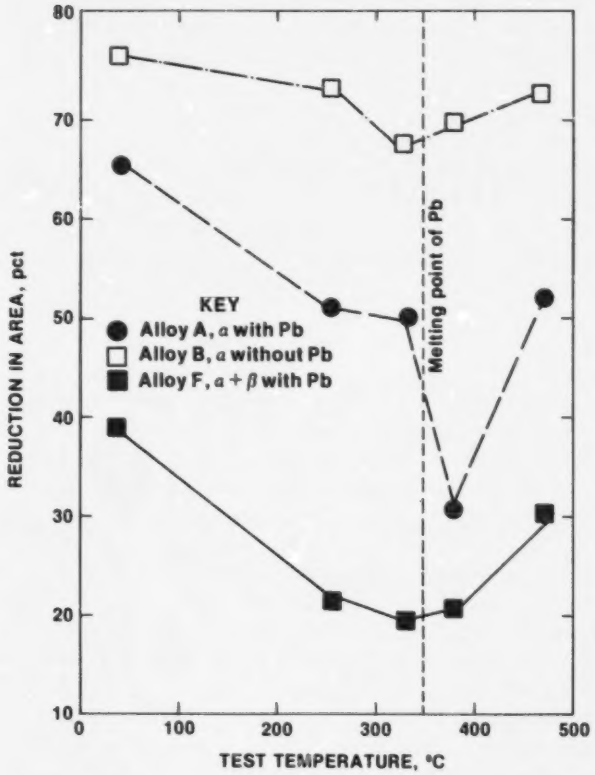

FIGURE 8. - Effect of lead on tensile ductility (reduction in area) of nickel-silvers (16).

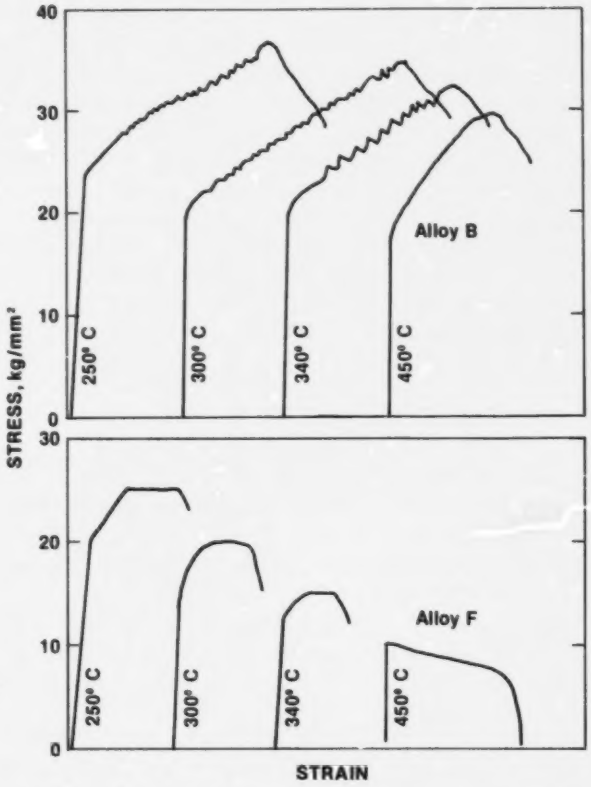

FIGURE 9. - Effect of lead on stress-strain behavior of nickel-silvers (alloy B; alpha alloy plus lead; alloy F; alpha plus beta alloy plus lead) (16).

Microprobe analysis was also conducted to show that there is a marked concentration of lead along the fissures of the advancing crack front during fire cracking. This further supported the liquid-metal embrittlement model.

Additional Studies

Other tests were conducted to study stress relaxation and desensitizing phenomena, the latter being related to dislocations piling against grain boundaries. The influence of storage time after cold work was also examined, as was the effect of lead on alloys of alloy A composition but with 0.2 and 2.5 wt pct Pb. Both these and the previously discussed results were related to the Griffith-Orowan fracture theory, leading to the following summary characteristics associated with alloys sensitive to fire cracking:

1. A second phase is present that melts during heat up, forming an embrittling couple with the alloy.
2. The melting point of the second phase must be low enough so that the residual stresses are relaxed only slightly when melting occurs.
3. High yield strength of the matrix alloy permits substantial buildup of the residual stresses.
4. The alloy must contain voids along the potential fracture path, thus eliminating the need for crack initiation.

It was not clear from Isler's study why the alloy with lead but no nickel (alloy G) was not sensitive to fire cracking.

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MICROSTRUCTURAL EFFECTS

Microstructural effects, such as solute element segregation at grain boundaries and phase relationships, were considered to some extent in the above discussions on hot workability and fire cracking. Other reported studies concentrated on microstructural evaluations to determine the effects of various elements on the microstructure of tin bronze and to determine the cause of failure of manganese-nickel-aluminum bronze cast propeller blades.

TIN BRONZES

Couture (9) studied a tin-bronze alloy (88 Cu-10Sn-2Zn) to determine the effects of nickel, phosphorus, iron, lead, antimony, sulfur, and silicon on microstructure. The alloy base composition and ranges of additions studied are listed in table 6. The purpose was to produce microstructures that would help explain the influence of these elements on the properties of tin bronzes investigated by other researchers. The observations made from micrographs are highlighted here.

TABLE 6. - Composition of tin bronze alloy used for microstructure studies, weight percent (8)

Element	Master alloy	Range of impurities
Cu.....	87.0	([1])
Sn.....	10.4	([1])
Zn.....	2.4	([1])
Fe.....	.017 -0.018	0.02- 1.88
Ni.....	.0015- .0018	.002-3.38
P.....	.003 - .004	.004-1.05
Pb.....	.004 - .005	.004-1.84
S.....	.004 - .005	.004- .030
Sb.....	.0016	.002-2.19
Si.....	.002	.002- .035

[1]The master alloy was used to make all subsequent melts with the various levels of impurities.

Metallography

Base Alloy

Microstructure consisted of the continuous copper-rich alpha phase (tin and zinc in solution) and pools of the alpha-delta eutectoid of tin bronzes.

Antimony

At 0.78 and 2.19 pct, antimony caused an increase in the amount and size of the delta phase. This was attributed to decreased solubility of tin as antimony goes into solid solution. Grain size was not affected.

Iron

At 1.88 pct Fe, the eutectoid pools in the cast structure were more abundant and coarser. The as-cast high-iron alloys also showed a fine precipitate around the eutectoid and a starlike constituent in the eutectoid, both presumably iron-rich. Heat treatment at 700° C (1,292° F) dissolved the delta phase and resulted in dense precipitation of a fine, iron-rich constituent throughout the matrix. Some grain refinement occurred, ranging from radially columnar at 0.48 pct Fe to equiaxed (0.5-mm-diameter) at 1.88 pct Fe.

Lead

Delta phase and grain size were not affected by lead additions. However, because of low solubility, lead particles concentrated in the eutectoid.

Nickel

Additions up to about 1 wt pct had no significant effect. At the 1.33- and 3.38-wt pct levels, however, the microstructure showed a more abundant delta phase in large clusters than was observed in the base copper-tin-zinc alloy. Alpha

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pools within the eutectoid were larger. Theta phase, though observed in nickel-containing bronzes by others, was not present in the alloys studied by Couture. Possible explanations for this difference are the absence of lead, lower nickel contents, and lack of equilibrium in the test specimens. Grain shape and size were also modified by nickel. Grains changed from radially columnar 3/8 in (9.5 mm) long to equiaxed grains 1/64 in (0.8 mm) in diameter at 3.38 wt pct nickel.

Phosphorus

Phosphorus contents of 0.1 to 1.05 wt pct resulted in an intermetallic compound presumed to be copper phosphide (Cu_3P), which at low concentrations was distributed mainly on the outside edges of the alpha and delta eutectoid, and at higher concentrations was distributed within the eutectoid and in adjacent areas of the matrix alpha phase. Phosphorus had no effect on grain size.

Silicon

Silicon additions resulted in a more abundant and coarser eutectoid. Grain size changed from columnar to equiaxed even at the low addition (0.005 pct). Grain size was reduced only slightly with further additions.

Sulfur

At all levels of addition, sulfur formed a large number of translucent dark gray, probably complex, sulfides. Grain size was not affected.

Microprobe Analysis

Microprobe analyses were conducted to determine the distribution of the impurity elements. Areas examined included the matrix (center of the dendrite arms), coring (surrounding the eutectoid), delta phase (or eutectoid pools in the cases of very small delta areas), and inclusions. The following qualitative results were obtained.

Iron

Iron was concentrated in the matrix. The iron concentration in the eutectoid was well below that of the sample average.

Nickel and Antimony

These were primarily associated with the eutectoid.

Sulfur

Larger inclusions were confirmed as sulfides.

Tin

Tin concentration in the matrix was below the alloy average. In the cored areas, it was similar to the average composition. The eutectoid showed about three times the average tin composition.

Zinc

Matrix and cored areas were about the same, owing to rapid zinc diffusion, which was greater than in the eutectoid.

Grain Size and Shape

Grain structure was changed from columnar to equiaxed with additions of nickel, iron, or silicon. The grain refinement achieved was much less than that obtained in other studies with zirconium. Grain size and shape were not affected by phosphorus, lead, antimony, or sulfur.

Eutectoid Composition

The binary copper-tin phase diagram predicts alpha plus epsilon as the equilibrium phases at room temperature for tin bronze alloys. The eutectoid decomposition of delta to alpha plus epsilon (350° C) is sluggish, however, and delta is retained down to room temperature. Although the delta would be expected to contain 32.6 pct Sn, the presence of more than 2 pct Zn and additional elements will alter the delta composition.

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Microsegregation

Metallographic examination revealed that phosphorus and lead segregated in or near the eutectoid as compounds or solid solutions and were present in the matrix between dendrite arms, thus confirming they segregated in the last-to-freeze liquid.

FAILURE ANALYSIS OF BRONZE PROPELLERS

As part of an extensive failure analysis program conducted on large propeller blades, Raymond (26) performed detailed microstructural analysis to determine cause of failure. Two 6-ton cast propeller blades failed while in service on a U.S. Coast Guard icebreaker. The alloy was a manganese-nickel-aluminum bronze, selected for excellent mechanical properties and good erosion and corrosion resistance in high-velocity seawater. Foundry and welding characteristics of the alloy are superior to those of conventional aluminum bronzes. When properly alloyed, a stable microstructure of approximately 50 pct alpha and 50 pct beta is obtained.

Composition

Chemical analyses were compared among samples from the failed blades and a good blade, and against the specification for MIL-B-21230 A, alloy 2 (table 7). The compositions all appeared to agree rather closely. However, a slightly higher concentration of chromium was noted in the samples from the failed blades. Although within the allowable maximum for "others," this small amount of chromium resulted in microsegregation, which led to an unstable microstructure, also causing a degradation of mechanical properties. For example, tensile strength, elongation, and Charpy V-notch energy were respectively 25, 50, and 75 pct lower than typical values.

Results of Analysis

The study reported by Raymond (26) involved a detailed analysis including microstructural analysis, mechanical property evaluation, thermal analysis, and fracture mechanics. The overall objective was to devise a corrective weld repair and heat treatment that would permit salvaging additional propeller blades. This was successfully accomplished. The overall analysis was rather detailed and beyond the scope of this paper. The studies to define the microstructural effects of chromium are highlighted here.

Chromium was isolated as the deleterious contaminant which formed an iron-rich dendritic phase ("sparkle") during solidification from the melt. A detailed ion microprobe mass analysis on a dendrite showed--

1. Dendrite was composed of iron, chromium, manganese, and only a small amount of nickel.
2. Surrounding phases were discontinuous alpha, richer in copper than the discontinuous beta, which was richer in manganese and iron.
3. Aluminum and nickel were uniformly distributed between the alpha and beta phases.

TABLE 7. - Chemical composition of propeller blades, weight percent (26)

Element	Failed blade 1	Failed blade 2	Good blade	MIL-B-21230A (alloy 2)
Cu	74.09	74.11	74.30	71 (min)
Mn	11.90	11.80	11.95	11-14
Al	7.77	7.82	7.90	7.0-8.5
Cr	.015	.016	.005	Not specified
Fe	3.42	3.28	3.10	2.0-4.0
Ni	2.42	2.59	2.51	1.5-3.0
Pb	<.004	<.0078	0	0.03 (max)
Si	.027	.041	.06	0.10 (max)
Others	0	0	0	0.05 (max)

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Based on these results, it was concluded that trace amounts of chromium caused the formation of iron-chromium-manganese dendrites at high temperatures. The surrounding matrix was thus depleted of (1) the manganese necessary to suppress eutectoid decomposition and (2) the iron necessary for fine grain structure. Manganese suppresses eutectoid decomposition because, being soluble in copper, it lowers the melting point of the alloy. The decomposition of eutectoid beta results in a brittle ternary phase, observed as fine lamellar precipitates in the beta phase. Two detailed heat treatments were devised for restoration of mechanical properties, both requiring that the eutectoid temperature of 675° C (1,250° F) be exceeded.

SUMMARY

The role of recycling copper alloys has been examined with regard to known metallurgical effects that result from excessive concentrations of alloying elements or impurities. A profile of the industry is briefly presented, followed by an overview of the reported metallurgical problems. A few of the problems were examined in more detail (case studies) for explanations of possible mechanisms and corrective procedures.

Wrought copper alloys are generally sensitive to even minor amounts of low-melting elements such as lead, bismuth, and antimony. Depending on the impurity, harmful effects have been observed for concentrations as low as 0.004 pct, although considerably higher concentrations can be tolerated for many of the alloys under appropriate processing conditions. The predominant effects are hot and cold shortness and fire-cracking tendency due to grain boundary segregation of such elements. Sensitivity to impurities is related to phase relationships, with single-phase alpha alloys being most sensitive. Certain other elements, including iron and silicon, may produce harmful effects, but in the case of iron can also counteract the harmful effects of low-melting impurities. Increased tolerance for otherwise harmful impurities is achieved also with additions of zirconium, rare earths, or uranium.

Cast alloys are considerably more tolerant of impurities than wrought alloys, although various impurities can have pronounced effects on castability and mechanical properties. Some of the elements known to adversely affect properties if not closely controlled include manganese, silicon, aluminum, iron, arsenic, antimony, lead, and bismuth. Small amounts of chromium (0.015 wt pct) caused serious failures in cast aluminum bronzes owing to preferential segregation and subsequent effects on transformation kinetics and brittle behavior.

Although the effects of impurities have been well defined for many alloy systems and adequate information seems to be available to reevaluate alloy specifications, it is important to note that definitive information is not available for all cases, owing to the complexity of some alloys and the interaction effects. The many processing variables and service conditions further prevent an understanding of impurity effects in commercial alloys.

A major objective of the Bureau of Mines recycling research has been to improve the efficiency of recycling by introducing new technologies to more accurately identify and sort scrap metals (3, 19-20, 27), thereby minimizing the chance of introducing tramp elements. The evidence clearly supports the often-expressed concern that scrap must be carefully and accurately segregated to avoid harmful impurity effects when recycled, but all metallurgical problems are not attributable solely to impurities. Care must also be exercised to assure that established metallurgical treatments are followed when processing recycled alloys and when putting them into service. Unfounded claims that processing or service failures are caused solely by impurities from scrap do not effectively serve the recycling industry, the scrap user, or the Nation when conservation measures such as recycling are so vitally needed in extending our mineral resources.

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